



# Issues and Consequences of Atomic Oxygen Undercutting of Protected Polymers in Low Earth Orbit

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## **ABSTRACT**

Hydrocarbon based polymers that are exposed to atomic oxygen in low Earth orbit are slowly oxidized which results in recession of their surface. Atomic oxygen protective coatings have been developed which are both durable to atomic oxygen and effective in protecting underlying polymers. However, scratches, pin window defects, polymer surface roughness and protective coating layer configuration can result in erosion and potential failure of protected thin polymer films even though the coatings are themselves atomic oxygen durable. This paper will present issues that cause protective coatings to become ineffective in some cases yet effective in others due to the details of their specific application. Observed in-space examples of failed and successfully protected materials using identical protective thin films will be discussed and analyzed. Proposed approaches to prevent the failures that have been observed will also be presented.

## **INTRODUCTION**

The use of atomic oxygen protective coatings applied over conventional polymers that have traditionally been used in space has been the primary approach to date to achieve atomic oxygen durability in space. Metal atoms or metal oxide molecules have been used extensively for the protective coating materials. Typically silicon dioxide, fluoropolymer filled silicon dioxide, aluminum oxide or germanium have been sputter deposited on polymers to provide atomic oxygen protection. For example, the large solar array blankets on International Space Station have been coated with 1300 Angstroms of SiO<sub>2</sub> for atomic oxygen protection [1].

Although protective coatings can provide excellent atomic oxygen protection of hydrocarbon or halocarbon polymers, the details of how the coatings are used and/or applied can result in widely varying protection consequences.

## IN-SPACE PROTECTIVE COATING EXPERIENCES

### European Retrievable Carrier (EURECA)

The EURECA spacecraft, which was deployed into low Earth orbit on August 2, 1992 and retrieved after 11 months on June 24, 1993, was exposed to an atomic oxygen fluence of approximately  $2.3 \times 10^{20}$  atoms/cm<sup>2</sup> [2]. To assist in its retrieval, the spacecraft used two thin adhesively mounted acrylic optical retroreflectors for laser range finding. Prevention of atomic oxygen attack of the retroreflector surfaces, which would have degraded the specularity of the reflectance, was accomplished by coating the retroreflector surface with a ~1000 Angstrom thick film of sputter deposited SiO<sub>2</sub> filled with 8% fluoropolymer (by volume). The LEO exposed and retrieved retroreflector was inspected and optically characterized. The results indicated that the protective coating provided excellent protection and the retroreflector performed as planned except in a small 3 cm patch where the protective coating was accidentally abraded prior to flight as a result of handling during preflight ground integration [3]. Figure 1 shows a close up picture of the retroreflectors as well as their appearance during illumination after retrieval.

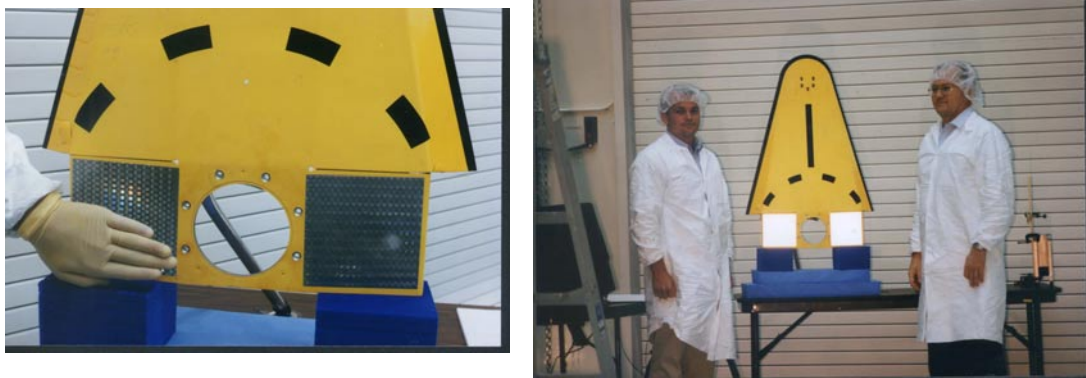


Figure 1.—EURECA retroreflectors after retrieval close up and during illumination.

### International Space Station (ISS) Retroreflectors

ISS retroreflectors, which serve in a similar role as the EURECA retroreflectors, have been used which employ a glass corner cube retroreflector that is housed in a 10 cm diameter Delrin® 100 polyoxymethylene mount. Polyoxymethylene is an oxygen rich polymer is readily attacked by atomic oxygen. To prevent atomic oxygen attack of the Delrin®, the machined polymer surfaces were coated by the same processes, in the same facility and with the same ~1000 Angstrom thin film of sputter deposited 8% fluoropolymer-filled SiO<sub>2</sub> that was used for the EURECA retroreflector. Several of these retroreflectors have been mounted on the external surfaces of the ISS structures at various locations that are exposed to LEO atomic oxygen. Figure 2 shows a close up of one of the coated retroreflectors prior to use on ISS in space as well as a photograph from space of a retroreflector after attack by atomic oxygen. It is clear from the in-space photograph that the coating was only partially attached allowing direct atomic oxygen attack of the unprotected areas.

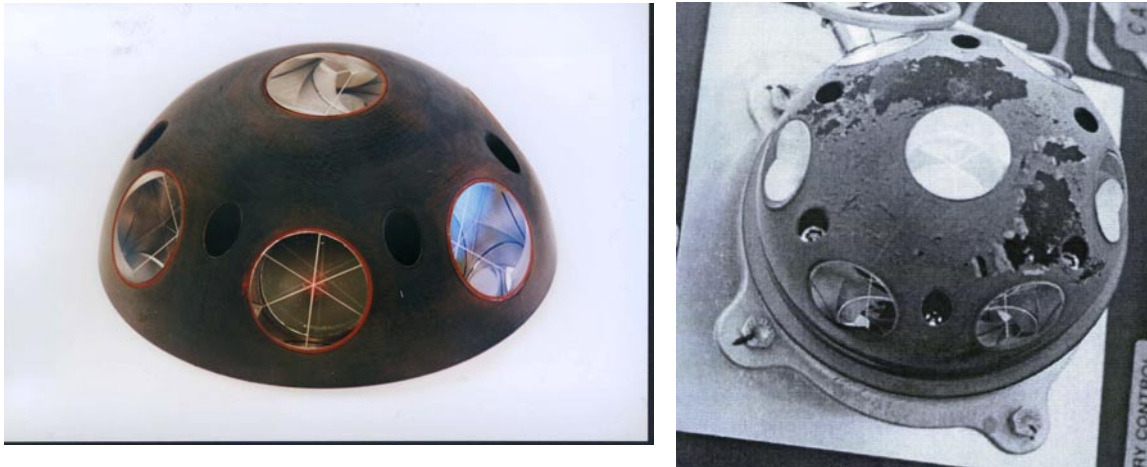


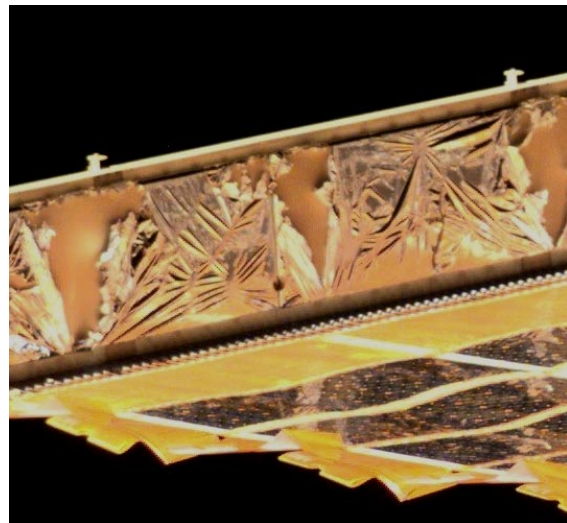
Figure 2.—ISS retroreflectors prior to launch and during use in space on ISS after atomic oxygen attack.

### ISS Photovoltaic Array Blanket Box Covers

Prior to deployment, the ISS photovoltaic arrays were folded into a box that allows the array to be compressed in a controlled manner against a cushion of open pore polyimide foam that was covered with a 0.0254 mm thick aluminized Kapton® blanket. The Kapton® was coated on both surfaces with 1000 Angstroms of vacuum deposited aluminum. The array was exposed to the LEO atomic oxygen environment from December 2000 through December 2001. Photographs of the array, taken in orbit, indicated that the Kapton® blanket had been almost completely oxidized leaving only the thin largely torn aluminization in place as shown in Figure 3.



a. Distant photo



b. Close up photo

Figure 3.—ISS photovoltaic array showing effects of atomic oxygen erosion of the double aluminized Kapton® blanket cover for the ISS photovoltaic arrays box

## ANALYSIS AND DISCUSSION

### Surface Roughness And Defect Density

The drastic differences in atomic oxygen protection provided by the same SiO<sub>2</sub> coating filled with 8% fluoropolymer on the EURECA retroreflectors and the ISS retroreflectors is thought to be due to drastic differences in the protective coating defect densities. The acrylic EURECA retroreflectors surfaces were extremely smooth as required to produce high fidelity specular reflections. Such smooth surfaces result in low-defect-density protective coatings that have also been demonstrated, in ground laboratory testing, to perform acceptably. For example smooth surface (air-cured side) Kapton® when coated with 1300 Angstrom thick SiO<sub>2</sub> resulted in ~ 400 pin window defects/cm<sup>2</sup>. However, the same coating on the rougher surface (drum-cured side) has been found to result in 3500 pin window defects/cm<sup>2</sup> [1]. Similar experiences with graphite epoxy composite surfaces formed by casting against another smooth surface produce defect densities of ~262,300 defects/ cm<sup>2</sup> [3]. Surface leveling polymers applied over such surfaces have been found to reduce the defect densities by an order of magnitude to ~22,000 defects/cm<sup>2</sup> [3].

The machining of the Delrin® 100 (polyoxymethylene) retroreflector mount surfaces produces machine marks or rills in the surface resulting in a highly defected atomic oxygen protective coating. Such rills allow atomic oxygen to oxidize and undercut the high erosion yield Delrin®, causing the coating to gradually be left as an unattached gossamer film over the retroreflector mount which could be easily torn and removed by intrinsic stresses and thruster plume loads. The use of smoother surfaces, surface-leveling coatings over the machined Delrin® or use of alternative atomic oxygen durable materials could potentially eliminate the observed problem.

### Trapping of Atomic Oxygen Between Defected Protective Surfaces

The lack of atomic oxygen protection provided by the aluminized Kapton® blanket cover for the ISS photovoltaic arrays box cushion is thought to be due to the trapping of atomic oxygen between the two aluminized surfaces on the 0.0254 mm thick Kapton® blanket. Defects in the space exposed aluminized surface allow atomic oxygen to erode undercut cavities. If the undercut cavity extends downward to the bottom aluminized surface, then the atomic oxygen becomes somewhat trapped and has multiple opportunities for reaction until it either recombines, reacts, or escapes out one of the defects in the aluminization. This eventually results in a complete loss of the Kapton® with only the aluminized thin film remaining. The vacuum deposited aluminum has a slight tensile stress that causes stress wrinkling of the unsupported aluminum films. Figure 4 is a photograph of a vacuum deposited aluminized Kapton® sample that was placed in a radio frequency plasma environment to completely oxidize the Kapton® over a portion of the sample.





Figure 4.—Photograph of a vacuum deposited aluminized Kapton® sample bonded to a metal frame after ground laboratory oxidation of the Kapton®.

As can be seen in Figure 4, where the ~1000 Angstrom aluminum film in the lower portion of the sample is free standing, stress wrinkles and tears develop similar to those seen in the ISS photograph of Figure 3.

A two dimensional Monte Carlo computational model has been developed which is capable of simulating LEO atomic oxygen attack and undercutting at crack defects in protective coatings over hydrocarbon polymers [4]. Optimal values of the atomic oxygen interaction parameters were identified by forcing the Monte Carlo computational predictions to match results of protected samples retrieved from the Long Duration Exposure Facility [4]. These interaction parameters and values were used to predict the consequences of atomic oxygen entering a 2-dimensional crack or scratch defect in the top aluminized surface. This was accomplished using 100,000 Monte Carlo atoms entering a defect which was 20 Monte Carlo cells wide (representing a 13.4 micrometer wide defect) over a 38 cell thick (representing a 0.0254 mm thick) Kapton® blanket. Figure 5 compares the Monte Carlo model computational erosion results for a 45-degree angle of attack (relative to the surface normal) of the atomic oxygen for both double surface-coated Kapton® (which was the case for ISS) and single top surface-coated Kapton®.



a. Aluminized on both sides

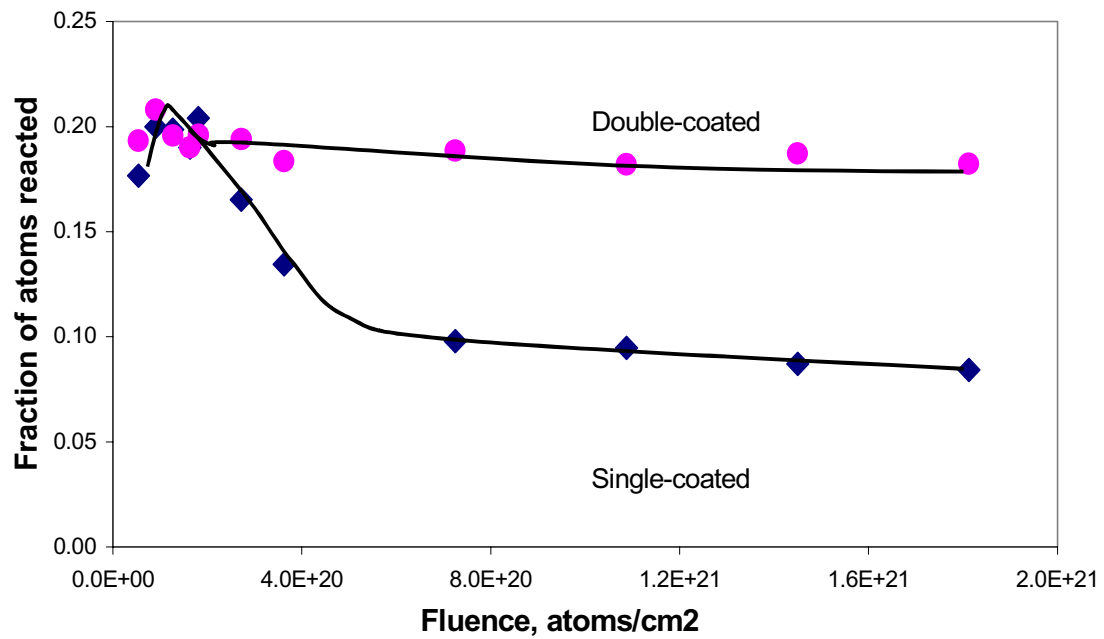


b. Aluminized on exposed side only

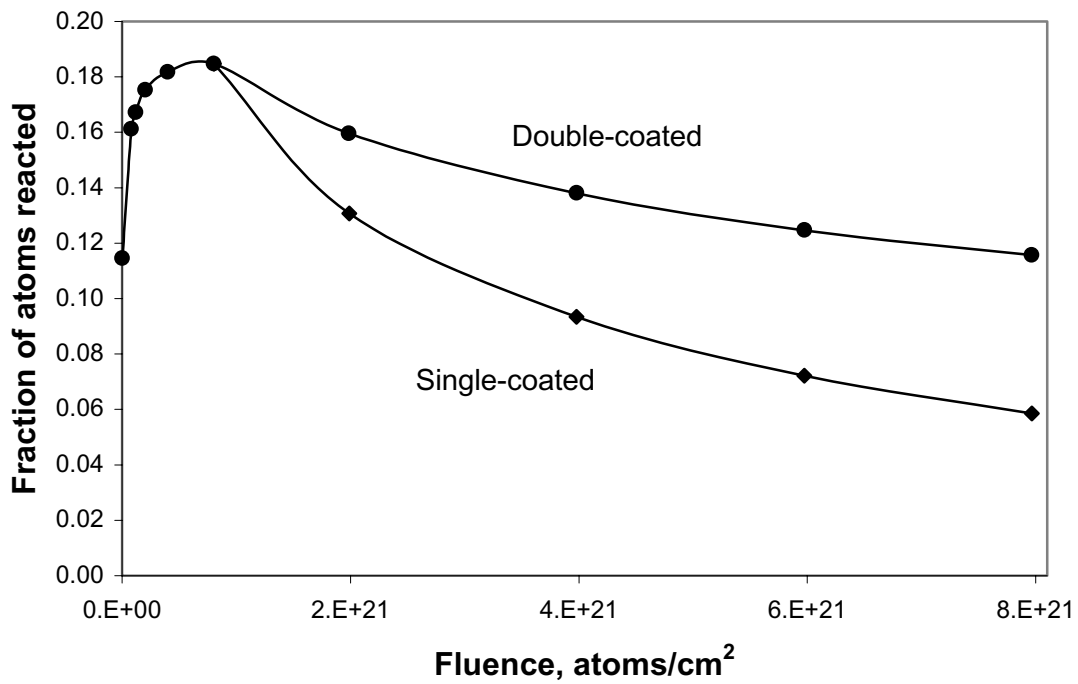
Figure 5.—Monte Carlo computational atomic oxygen erosion predictions for a 45 degree from perpendicular angle of attack of atomic oxygen at a crack or scratch defect in the aluminized Kapton® surface.

As can be seen from Figure 5, even though the atomic oxygen gradually becomes less energetic with the number of interactions and has approximately a 13% chance of recombination, the trapped atoms undercut far more in the actual ISS case of a double aluminization as would have occurred if the Kapton® was simply aluminized on one side. Thus, contrary to intuition, the use of two atomic oxygen protective coatings rather than a single coating appears to cause more rather than less undercutting attack.

The extent of undercutting of trapped atomic oxygen is also dependent on the opportunity for the atoms to loose energy, recombine, or escape back out the defect opening. Figure 6 compares the results of 2-dimensional Monte Carlo modeling and 3- dimensional pin-window computational predictions [5] for a 45-degree angle of attack atomic oxygen of a 13.4 micrometer wide crack or scratch for the 2-dimensional case and a 5.1 micrometer diameter circular aperture for the 3- dimensional case for both single side and double side aluminized Kapton®.



a. 2-Dimensional model of crack or scratch defect



b. 3-Dimensional model of circular pin window defect

Figure 6.—Computational atomic oxygen erosion predictions for 45-degree incident atomic oxygen attack at defect sites protected Kapton®.

As can be seen in Figure 6, for both 2-dimensional modeling of a crack or scratch defect and 3-dimensional modeling of a circular defect the growth characteristics of the under cut cavity have similar trends with fluence. Initially, as the undercutting starts the existence or absence of the back surface coating plays no role and as the cavity grows the probability of atoms reacting increases due to trapping of the incoming atom. However, as the bottom surface is reached, atoms begin either to escape, or in the case of no back-surface coating, they recombine after collision with the  $\text{SiO}_2$  on the back surface. The double surface aluminized Kapton® consistently reacts more atomic oxygen atoms than the single surface aluminized Kapton® except at very low fluences where the erosion in either case does not reach the bottom of the polymer. For both cases, as the fluence increases, the atomic oxygen can escape out the bottom (only in the case of the single surface aluminized Kapton®), recombine, or thermally accommodate and thus becomes less probable to react with the Kapton®. Thus it appears that a single surface aluminized Kapton® would have been much more durable because the unreacted atoms passing through the bottom of the polymer would simply enter into the open pore foam and gradually react with it, without causing much damage to the aluminized Kapton®.

The double- $\text{SiO}_2$  coated ISS solar array blankets may show similar detachment of the outer surface  $\text{SiO}_2$  layer with time. However, the defect density appears to be much lower than for vacuum deposited aluminum coatings as shown in Figure 7 which compares the experimental results of RF plasma oxidation of double aluminized Kapton® with double  $\text{SiO}_2$  coated Kapton®.

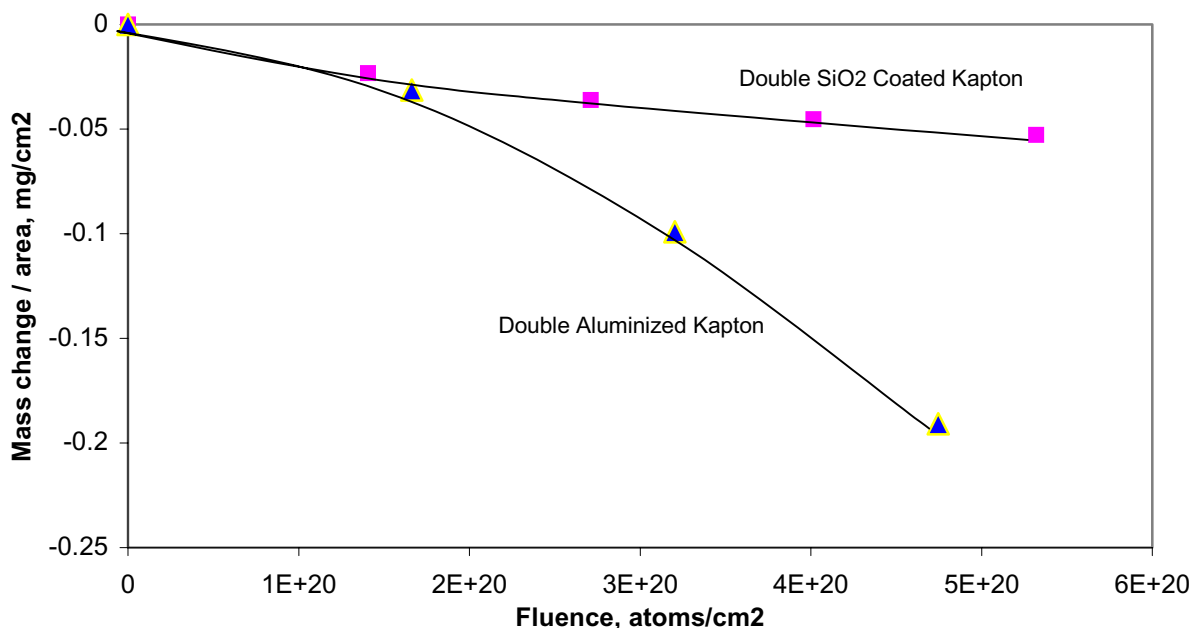


Figure 7.—Comparison of RF plasma oxidation of aluminized and  $\text{SiO}_2$  coated Kapton®.

## CONCLUSIONS

Atomic oxygen protective coatings have been developed and used in space that perform acceptably. However, rough surface substrates cause defects in the protective coatings that allow atomic oxygen to react and gradually undercut the protective coating. In the case of machined Delrin® ISS retroreflector mounts, such roughness has lead to detachment of portions of the protective film covering the retroreflector mount.

Atomic oxygen undercutting of the double aluminized Kapton® blanket covers for the ISS photovoltaic array box cushions has occurred resulting in a torn and partially detached aluminum film. Based on computational modeling, atomic oxygen atoms that become trapped between the two aluminized films on each side of the Kapton® blanket appear to cause accelerated undercutting damage in comparison to the use of a single top-surface coating.

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